N O T I C E

THIS DOCUMENT HAS BEEN REPRODUCED FROM MICROFICHE. ALTHOUGH IT IS RECOGNIZED THAT CERTAIN PORTIONS ARE ILLEGIBLE, IT IS BEING RELEASED IN THE INTEREST OF MAKING AVAILABLE AS MUCH INFORMATION AS POSSIBLE

9950·64

DOE/JPL -956045 - 81/2

DISTRIBUTION CATEGORY UC-63

SILICON PRODUCTION PROCESS EVALUATIONS

QUARTERLY TECHNICAL PROGRESS REPORT (II)

Issue Date: December, 1981

Reporting Period: Aug. 1 - Oct. 31, 1981

TREI

Texas Research and Engineering Institute, Inc.

P.O.Box 9

Fort Neches, Texas 77651

JPL Contract No. 956045

Contractual Acknowledgement

The JPL Flat-Plate Solar Array (FSA) Project is sponsored by the U.S. Department of Energy and forms part of the Solar Photovaltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays. This work was performed for the Jet Propulsion Laboratory, California Institute of Technology by agreement between NASA and DOE.

ABSTRACT

Chemical engineering analysis of the HSC process (Hemlock Semiconductor Corporation) for producing silicon from dichlorosilane in a 1,000 MT/yr plant was continued during this reporting period.

Progress and status for the chemical engineering analysis of the HSC process are reported for the primary process design engineering activities: base case conditions (85%), reaction chemistry (85%), process flow diagram (60%), material balance (60%), energy balance (30%), property data (30%), equipment design (20%) and major equipment list (10%).

Engineering design of the initial distillation column (D-01, stripper column) in the process was initiated. The function of the distillation column is to remove volatile gases (such as hydrogen and nitrogen) which are dissolved in liquid chlorosilanes. Initial specifications and results for the distillation column design are reported including the variation of tray requirements (equilibrium stages) with reflux ratio for the distillation.

TABLE OF CONTENTS

I. CHEMICAL ENGINEERING ANALYSIS

During this reporting period, chemical engineering analysis of the HSC process (Hemlock Semiconductor Corporation) for producing silicon from dichlorosilane was continued.

Progress and status for the chemical engineering analysis are summarized below for the primary engineering activities:

	Prior	Current
1. Base Case Conditions	60%	85%
2. Reaction Chemistry	50%	85%
3. Process Flow Diagram	35%	60%
4. Material Balance	35%	60%
5. Energy Balance	10%	30%
6. Property Data	10%	30%
7. Equipment Design	5%	20%
8. Major Equipment List	0%	10%

Table I-1 presents status details for the chemical engineering analysis involving the preliminary process engineering design of a 1,000 MT/yr plant for solar cell grade silicon via the HSC process.

The base case conditions for the process are given in Table I-2 including process technology descriptions applicable to the silicon tetrachloride hydrogenation unit; dichlorosilane production and purification unit; and dichlorosilane decomposition and recovery unit. This version of the base case conditions includes the initial process technology descriptions for the distillations (D-01, D-02 and D-03) involved in the dichlorosilane production and purification.

The reaction chemistry for the HSC process is shown in Table I-3. In the waste treatment, lime is used in aqueous solution to neutralize the various waste streams. This version of the reaction chemistry is essentially identical to that reported earlier. Some updating may be required as data becomes available from silicon deposition with larger sized rods.

The process flowsheet for the HSC process is presented in Figure I-1. The process flowsheet is based on quarterly reports (Figures 5, 6 and 7 of ref. A5) of Hemlock Semiconductor Corporation. The process flowsheet as shown is a conceptual type and summarizes the primary unit operations involved in silicon tetrachloride hydrogenation, dichlorosilane production-purification and dichlorosilane decomposition-recovery units of the plant.

In the process, the reaction product issuing from the hydrochlorination reactor (hydrochlorination-hydrogenation reaction) undergoes a vapor-liquid flash separation. The vapor fraction containing the hydrogen from the flash is recycled back to the hydrochlorination reactor. The liquid fraction containing the chlorosilanes and dissolved gases is fed to the initial distillation column.

Engineering design of the initial distillation column (D-01, stripper column) in the process was initiated during this reporting period. The function of the distillation column is to remove volatile gases (such as hydrogen and nitrogen) which are dissolved in liquid chlorosilanes. For the engineering design, trichlorosilane was selected as the heavy key component for the separation. Additional details for the design including specifications and results for the column are given in the Appendix (Appendix A1 and A2).

The design results for number of trays (equilibrium stages) required for the separation are shown in Figure I-2. The design curve in the figure discloses the variation of number of trays with reflux ratio for the distillation.

During this reporting period, additional communications and discussions were conducted with Hemlock Semiconductor Corporation concerning the flowsheet and base case conditions for the HSC process. Near the end of the reporting period, an updated version of the process flowsheet and base case conditions was received (ref. A5a).

Table I-1

CHEMICAL ENGINEERING ANALYSIS:

PRELIMINARY PROCESS DESIGN ACTIVITIES FOR HSC PROCESS

Prel. Process Design Activity	Status
1. Specify Base Case Conditions	◐
1. Plant Size	◐
2. Product Specifics	◐
3. Additional Conditions	◐
2. Define Reaction Chemistry	◐
1. Reactants, Products	◐
2. Equilibrium	◐
3. Process Flow Diagram	◐
1. Flow Sequence, Unit Operations	◐
2. Process Conditions (T, P, etc.)	◐
3. Environmental	◐
4. Company Interaction (Technology Exchange)	◐
4. Material Balance Calculations	◐
1. Raw Materials	◐
2. Products	◐
3. By-Products	◐
5. Energy Balance Calculations	◐
1. Heating	◐
2. Cooling	◐
3. Additional	◐

Prel. Process Design Activity	Status
6. Property Data	◐
1. Physical	◐
2. Thermodynamic	◐
3. Additional	◐
7. Equipment Design Calculations	◐
1. Storage Vessels	◐
2. Unit Operations Equipment	◐
3. Process Data (P, T. rate, etc.)	◐
4. Additional	◐
8. List of Major Process Equipment	◐
1. Size	◐
2. Type	◐
3. Materials of Construction	◐
9. Production Labor Requirements	O
1. Process Technology	O
2. Production Volume	O
10. Forward for Economic Analysis	O

O Plan
◐ In Progress
● Complete

TABLE I-2

BASE CASE CONDITIONS FOR HSC PROCESS

1. Plant Size
   - Silicon produced from dichlorosilane (DCS)
   - 1000 metric tons/yr of silicon
   - High purity silicon
   - Final product form (solid rods)

2. Hydrogenation Reaction
   - Metallurgical grade silicon, hydrogen, and recycle silicon tetrachloride (TET) used to produce trichlorosilane (TCS)
   - Copper catalyzed
   - Fluidized bed
   - 500°C, 514.7 psia
   - 29.5% conversion to TCS (example)

3. Recycle For Hydrogenation Unit
   - Unreacted hydrogen from hydrogenation reactor is seperated from chlorosilanes by condensation and then recycled
   - Unreacted silicon tetrachloride (TET) is seperated by distillation and recycled

4. Distillation, D-01
   - Stripper column handles crude liquid chlorosilanes from hydrogenation
   - Removes volatile gases which are dissolved in the liquid chlorosilanes (such as H_2, N_2, HCl, etc.)

5. Distillation, D-02
   - Distillation column separates trichlorosilane (TCS) and silicon tetrachloride (TET)
   - Column has three feeds: stripper column bottoms, redistribution reactor chlorosilanes and chlorosilanes from the recovery unit (chlorosilanes from the silicon deposition reactors)

6. Distillation, D-03
   - Distillation column separates dichlorosilane (DCS) and trichlorosilane (TCS)
   - Column has one feed which is chlorosilanes from the boron removal unit
   - Overhead stream as the feed to CVD reactor
   - Bottom stream as the feed to redistribution reactor

7. Boron Removal
   - Removal of BCl_3 by complexation with nitrogen or oxygen base chemical which is supported on non-volatile substance
   - Fixed bed unit
   - No chlorosilane material loss

8. TCS Redistribution Reaction
   - TCS is redistributed to DCS and TET through catalytic reaction
   - Catalytic redistribution of TCS with amine function ion exchange resin (Dowex Ion Exchange Resin MWA-1)
   - Liquid phase 80 psia, 80C
   - Conversion from pure TCS feed is about 10.5% to DCS

TABLE I-2 (CONTINUED)

9. Chemical Vapor Deposition Reaction
   - -Silicon production
   - -Siemens CVD reactor (modified)
   - -Dichlorosilane and Hydrogen feed
   - -Molar conversion to silicon of 40%
   - -Deposition rate of 3000 g/hr
   - -Reactor exhaust gas composition (per mole of DCS fed)

HCl	.14
DCS	.10
TCS	.34
STC	.16

10. Recycle From CVD Reactor
    - -Chlorosilanes are recovered from a refrigeration process
    - -Hydrogen is seperated from HCl by adsorption process and recycled back to the CVD reactor
    - -Hydrogen chloride (HCl) is recovered as a salable by-product.

11. Slim Rod Pullers
    - -Prepare slim rods (small filaments)
    - -Slim rods used in Siemen's CVD reactor for silicon deposition
    - -Slim rod diameter of 6mm (approx. ¼ inch)

12. Operating Ratio
    - -Approximately 85% utilization (on stream time)
    - -Approximately 7445 hour/year production

13. Storage Consideration
    - -Feed materials (several days supply)
    - -Product (two shifts storage)
    - -Process (several hours to 1 shift)

14. Wastes Treatment
    - -Scrub and neutralize waste gas streams
    - -Caustic solution used to neutralize

TABLE 1-3

REACTION CHEMISTRY FOR HSC PROCESS

1. Hydrochlorination Reaction

$$3SiCl_4 + Si + 2H_2 \rightleftarrows 4SiHCl_3$$

2. Redistribution Reaction

$$2SiHCl_3 \rightleftarrows SiH_2Cl_2 + SiCl_4$$

3. Waste Treatment (representative - overall)

$$SiH_2Cl_2 + Ca(OH)_2 \xrightarrow{aq.} SiO_2 + CaCl_2 + 2H_2O$$

$$SiHCl_3 + 1.5Ca(OH)_2 \xrightarrow{aq.} SiO_2 + 1.5CaCl_2 + 2H_2O$$

$$SiCl_4 + 2Ca(OH)_2 \xrightarrow{aq.} SiO_2 + 2CaCl_2 + 2H_2O$$

4. Decomposition Reaction

$$SiH_2Cl_2 + H_2 \rightarrow Si + \text{By-Products}$$

Note:

1. Reaction 1 product contains H_2, HCl, $SiCl_4$, $SiHCl_3$, SiH_2Cl_2 (trace), other trace chlorides
2. Reaction 2 product contains $SiHCl_3$, $SiCl_4$, SiH_2Cl_2, SiH_3Cl
3. By-products in reaction 4 include H_2, HCl, SiH_2Cl_2, $SiHCl_3$ and $SiCl_4$

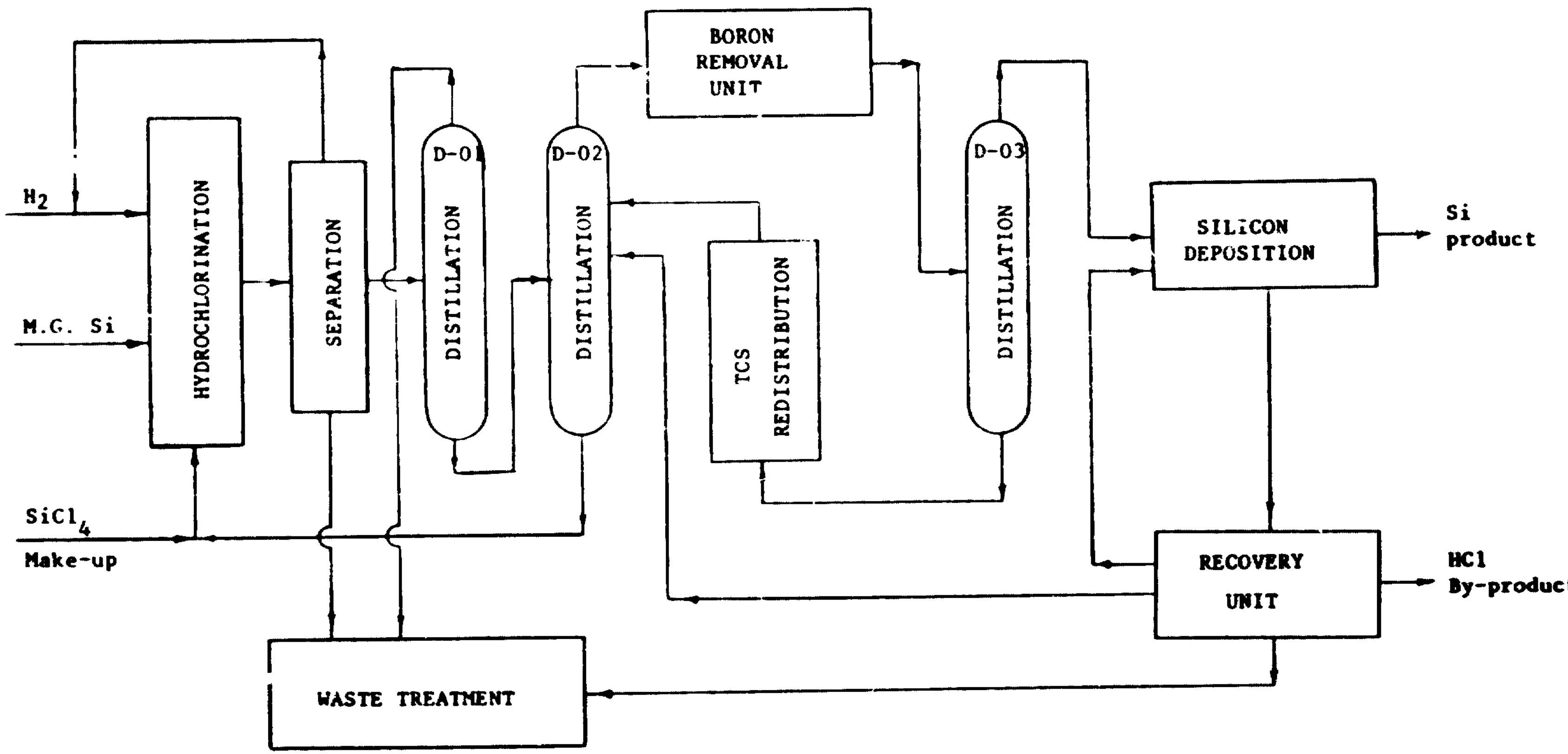

Figure I-1 Process Flowsheet for HSC Process

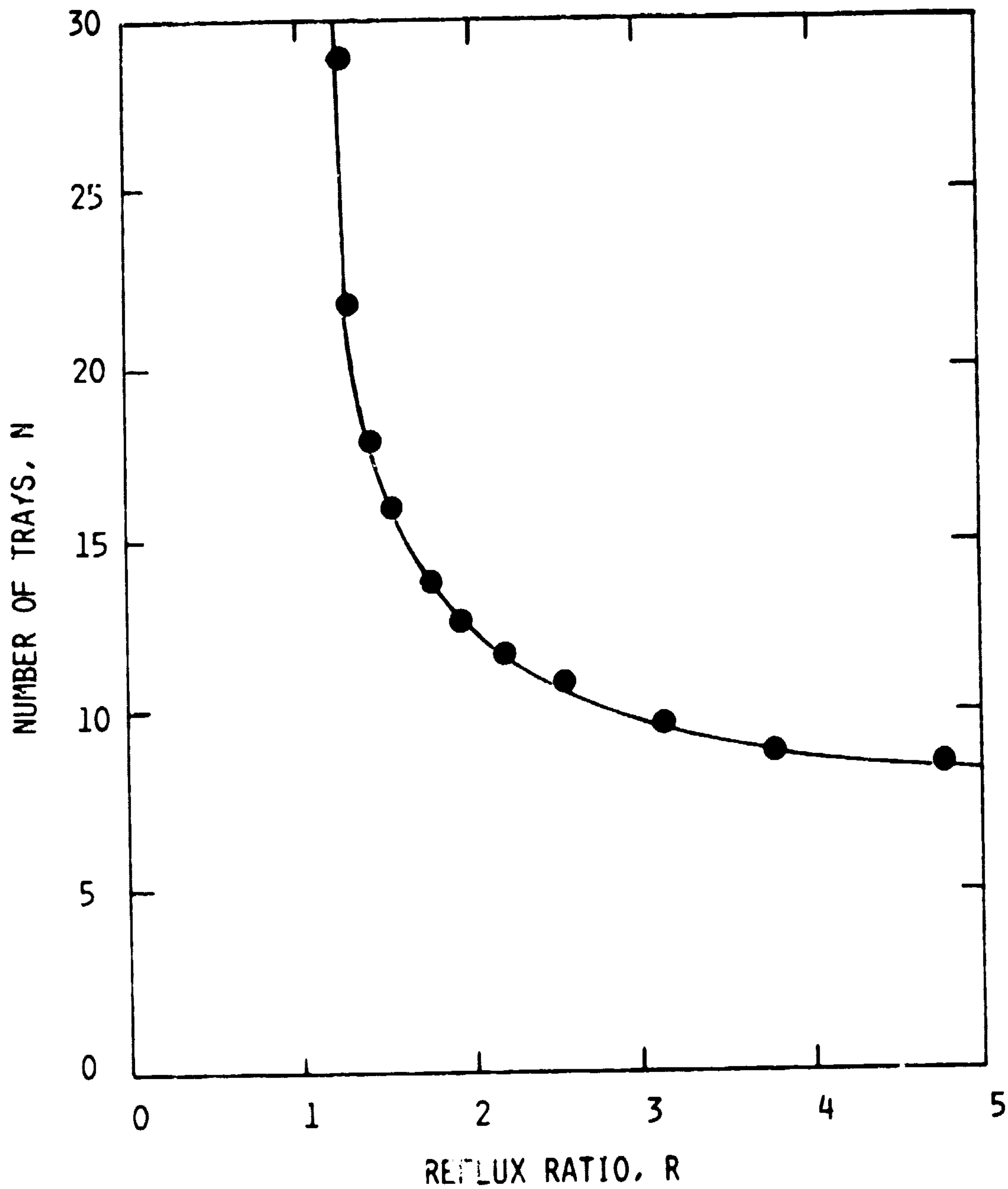

Figure I-2 Design Curve for Distillation, D-01

II. SUMMARY - CONCLUSIONS

Based on accomplishments during this reporting period, the following summary-conclusions are made:

1. Chemical engineering analysis of the HSC process (Hemlock Semiconductor Corporation) for producing silicon from dichlorosilane was continued.

2. Additional communications and discussions were conducted with Hemlock Semiconductor Corporation in regard to the process flowsheet. An updated version of flowsheet was received near the end of the reporting period.

3. Progress and status for the chemical engineering analysis of the HSC process are reported for the primary process engineering activities: base case conditions (85%), reaction chemistry (85%) process flow diagram (60%), material balance (60%), energy balance (30%), property data (30%), equipment design (20%) and major equipment list (10%).

4. Engineering design of the initial distillation column (D-01, stripper column) in the process was initiated. The function of the distillation column is to remove volatile gases (such as hydrogen and nitrogen) which are dissolved in liquid chlorosilanes. Initial specifications and results for the distillation column design are reported including the variation of tray requirements (equilibrium stages) with reflux ratio for the separation.

III. PLANS

Plans for the next reporting period are summarized below:

1. Continue chemical engineering analysis of the HSC process (Hemlock Semiconductor Corporation) for silicon.

2. For the preliminary process design, major efforts will be devoted to:

   - base case conditions
   - reaction chemistry
   - process flow diagram
   - material balance
   - energy balance
   - equipment design
   - major equipment list

3. Initiate economic analysis of the HSC process.

REFERENCES

References A (Hemlock Semiconductor Corporation)

A1. McCormick, J. R., A. Arvidson, F. Plahutnik, D. Sawyer and K. Sharp. "Development of A Polysilicon Process Based On Chemical Vapor Deposition", 1st Quarterly Progress Report, DOE/JPL 955533-79-1, Hemlock Semiconductor Corp. (January, 1980)

A2. Sharp, K., A. Arvidson, F. Plahutnik, and D. Sawyer, "Development Of A Polysilicon Process Based on Chemical Vapor Deposition", 2nd Quarterly Progress Report, DOE/JPL 955533-79-2, Hemlock Semiconductor Corp. (May, 1980)

A3. Sharp. K., A. Arvidson, F. Plahutnik, and D. Sawyer, "Development Of A Polysilicon Process Based On Chemical Vapor Deposition", 3rd Quarterly Progress Report, DOE/JPL 955533-79-3, Hemlock Semiconductor Corp. (August, 1980)

A4. Sharp. K., A. Arvidson, and D. Sawyer, "Development Of A Polysilicon Process Based On Chemical Vapor Deposition", 4th Quarterly Progress Report, DOE/JPL 955533-80-4, Hemlock Semiconductor Corp., (December, 1980)

A5. McCormick, J. R., K. Sharp, A. Arvidson and D. Sawyer, "Development Of A Polysilicon Process Based On Chemical Vapor Deposition", 5th Quarterly Progress Report, DOE/JPL 955533-79-5, Hemlock Semiconductor Corp. (March, 1981)

A5a. Plahutnik, F., Personal Communication, Correspondence Containing HSC Process Flowsheet Update and Base Case Conditions Changes, (Oct. 2, 1981)

References B (Union Carbide Corporation)

B1. "Feasibility Of The Silane Process For Producing Semiconductor-Grade Silicon", Final Report, JPL Contract 954334, Union Carbide Corporation (June, 1979)

B2. "Experimental Process System Development Unit For Producing Semiconductor-Grade Silicon Using the Silane-To-Silicon Process", 16th Quarterly Progress Report, DOE/JPL 954334-79/16, Union Carbide Corporation (July-Sept,1980)

B3. "Experimental Process System Development Unit For Producing Semiconductor-Grade Silicon Using The Silane-To-Silicon Process", 17th Quarterly Progress Report, Doe/JPL 954334-79/17, Union Carbide Corporation (Oct-Dec,1980)

B4. "Experimental Process System Development Unit For Producing Semiconductor-Grade Silicon Using The Silane-To-Silicon Process", 18th Quarterly Progress Report, DOE/JPL 954334-79/18, Union Carbide Corporation (Jan-March, 1981)

B5. "Experimental Process System Development Unit For Producing Semiconductor-Grade Silicon Using the Silane-To-Silicon Process", 19th Quarterly Progress Report, DOE/JPL 954334-79/19, Union Carbide Corporation (Apr-June, 1981)

References C (MIT - Massachusetts Institute of Technology)

C1. Mui, J. Y. P. and D. Seyferth, "Investigation Of The Hydrogenation of $SiCl_4$", 1st Quarterly Progress Report, DOE/JPL 955382-79/1, MIT (July, 1979)

C2. Mui, J. Y. P. and D. Seyferth,"Investigation Of The Hydrogenation Of $SiCl_4$", 2nd Quarterly Progress Report, DOE/JPL 955382-79/2, MIT (Ocotober, 1979)

C3. Mui, J. Y. P. and D.Seyferth, "Investigation Of The Hydrogenation Of $SiCl_4$", 3rd Quarterly Progress Report, DOE/JPL 955382-79/3, MIT (January, 1980)

C4. Mui, J. Y. P. and D. Seyferth,"Investigation Of The Hydrogenation Of $SiCl_4$", 4th Quarterly Progress Report, DOE/JPL 955382-79/4, MIT (April,1980)

C5. Mui, J. Y. P. and D. Seyferth, "Investigation Of The Hydrogenation Of $SiCl_4$", 5th Quarterly Progress Report, DOE/JPL 955382-79/5, MIT (July, 1980)

C6. Mui, J. Y. P. and D. Seyferth, "Investigation Of The Hydrogenation Of $SiCl_4$", 6th Quarterly Progress Report, DOE/JPL 955382-79/6, MIT (October, 1980)

C7. Mui, J. Y. P. and D. Seyferth, "Investigation Of The Hydrogenation Of $SiCl_4$", 7th Quarterly Progress Report, DOE/JPL 955382-79/7, MIT (January, 1981)

C8. Mui, J. Y. P. and D. Seyf rth, "Investigation Of The Hydrogenation Of $SiCl_4$", Final Report, JPL Contract 955382, DOE/JPL 955382-79/8, MIT (April, 1981)

APPENDIX A1

PROCESS ENGINEERING: DESIGN SPECIFICATIONS FOR DISTILLATION, D-01

Date 9/30/81

Issue No. Issue 1

1. Process Equipment Name Distillation, D-01 (Stripper Column)

2. Process Equipment Function Removes volatile gases from liquid chlorosilanes

3. Feed Specifications
   1. No. of Feeds 1
   2. No. of Feed Components 8
   3. Feed Components H_2, N_2, SiH_4, HCl, MCS, DCS, TCS, TET
   4. Feed Concentration See Item 7 below
   5. Feed Temperature 100F (37.8C) from ref. B1
   6. Feed Pressure 90 psia
   7. Light Key - LK Hydrogen Chloride, HCl
   8. Heavy Key - HK Trichlorosilane, $SiHCl_3$ (TCS)

4. Distillate Specifications
   1. Recovery of Light Key (LK) in Distillate 99.99 plus %
   2. Concentration Spec. low chlorosilanes

5. Bottoms Specifications
   1. Recovery of Heavy Key (HK) in Bottoms 99.95 %
   2. Concentration Spec. low volatile gases

6. General Specifications
   1. Pressure for Distillation 90 psia
   2. Condenser Type partial

      Vapor from top tray is cooled and collected in accumulator. Liquid from accumulator is returned to column as reflux. Vapor from accumulator is overhead distillate for the column.

APPENDIX A1

(Continued)

7. Feed Concentration

	Component	Feed Conc. x_{Fi}
	1. H_2	.020568
	2. N_2	.000019
	3. SiH_4	.000003
LK	4. HCl	.000496
	5. SiH_3Cl, MCS	.000064
	6. SiH_2Cl_2, DCS	.005819
HK	7. $SiHCl_3$, TCS	.249774
	8. $SiCl_4$, TET	.723256
		1.000000

NOTE:

1. Feed concentration is from ref. B1 (Union Carbide Final Report), pg. 212 (flowsheet, stream 125) and pg. E-9 (stream 125 composition, issue 2)

$$x_{Fi} = \frac{fi}{F} = \frac{\text{moles of i in feed}}{\text{total moles}}$$

APPENDIX A2

PROCESS ENGINEERING: DESIGN RESULTS FOR DISTILLATION, D-01

Date 10/8/81

Issue No. Issue 1

1. Process Equipment Name Distillation, D-01 (Stripper Column)

2. Equipment Specifications
   1. No. of Equilibrium Trays N = 13
   2. No. of Equilibrium Feed Tray N_F = 9
   3. Tray Efficiency 50 %
   4. No. of Actual Trays N_{actual} = 26
   5. No. of Actual Feed Tray $N_{F,actual}$ = 18
   6. Tray Spacing 18 in.
   7. Type of Tray Sieve
   8. Column Diameter 1.5-2 (use) ft.
   9. Column Height 39 ft.+ends ft.
   10. Reflux Ratio R = 1.90
   11. Design Temp. Top = -29 C (-21F)
       Bottom = 117 C (242F)
   12. Design Pressure 90 psia
   13. Materials of Construction 3/2 nickel steel

3. Product Specifications
   1. Feed Specifications
      1. Feed Concentration See Item 7 of Design Spec.
      2. Light Key - LK Hydrogen Chloride, HCl
      3. Heavy Key - HK Trichlorosilane, $SiHCl_3$ (TCS)
   2. Distillate Specifications
      1. Recovery of Light Key (LK) in Distillate 99.99 Plus %
      2. Concentration Spec. Low Chlorosilanes
   3. Bottoms Specifications
      1. Recovery of Heavy Key (HK) in Bottoms 99.95 %
      2. Concentration Spec. Low Volative Gases

APPENDIX A2

(Continued)

4. Results for Number of Trays

Reflux Ratio, R	No. of Equil. Trays, N	No. of Actual Trays, N_{actual}
1.28	29	58
1.31	22	44
1.40	18	36
1.53	16	32
1.78	14	28
1.91	13	26
2.23	12	24
2.54	11	22
3.18	10	20
3.82	9	18
4.77	9	18

5. Results for Stream Concentrations

	Component	Concentration		
		Feed	Distillate	Bottoms
	1. H_2	.020568	0.9510	1.154×10^{-6}
	2. N_2	.000019	0.0009	1.239×10^{-10}
	3. SiH_4	.000003	0.0002	1.206×10^{-8}
LK	4. HCl	.000496	0.0230	7.152×10^{-6}
	5. SiH_3Cl, MCS	.000064	0.0026	9.952×10^{-6}
	6. SiH_2Cl_2, DCS	.005819	0.0263	0.0055
HK	7. $SiHCl_3$, TCS	.249774	0.0036	0.2552
	8. $SiCl_4$, TET	.723256	9.607×10^{-6}	0.7393

F = 1
D = .02163
B = .97837

MILESTONE CHART